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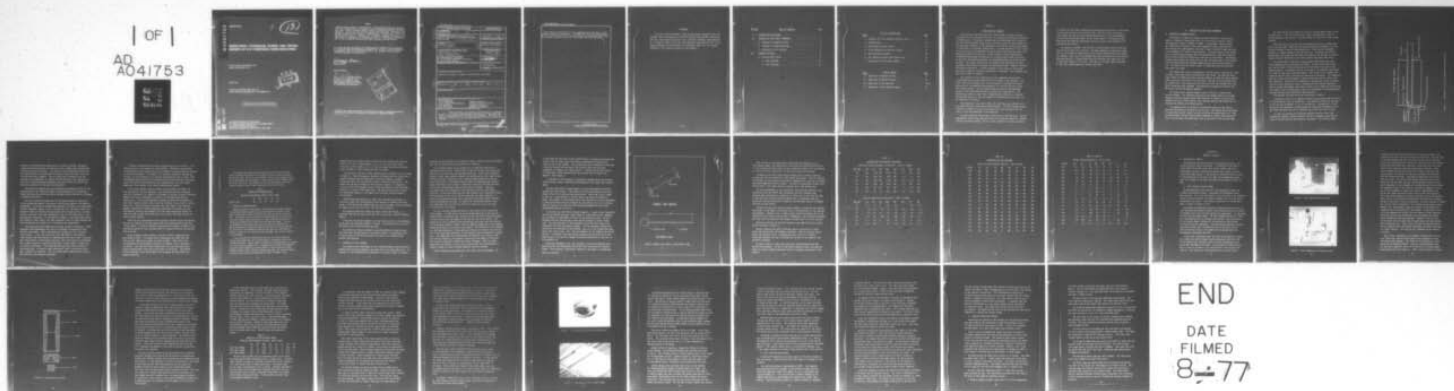APR 77   G N WEBB              F33615-73-C-4013

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# PURIFICATION, CONTROLLED DOPING AND CRYSTAL GROWTH OF II-VI COMPOUND SEMICONDUCTORS

*EAGLE-PICHER INDUSTRIES, INC.*
*MIAMI, OKLAHOMA 74354*

APRIL 1977

TECHNICAL REPORT AFML-TR-77-39
FINAL REPORT DECEMBER 1974 - NOVEMBER 1976

Approved for public release; distribution unlimited

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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*Lawrence C. Greene*

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Project Monitor


FOR THE DIRECTOR

WILLIAM G. D. FREDERICK, Chief
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The synthesis of various ultra high purity compounds of the II-VI group of semiconductor materials is described and tables of analytical data for each are included. The level of impurity concentration in synthesized ZnSe has been significantly lowered.

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The growth of crystals of II-VI compounds from the melt in the pressure furnace is reported. Included are data concerning doping of melt grown crystals with various amounts of selected impurities. The overall quality of the melt grown ZnSe has been improved.

## FOREWORD

This Final Technical Report, covering the period 1 December 1974 to 30 November 1976, was prepared by the Miami Research Laboratories, Electronics Division, Eagle-Picher Industries, Inc., at Miami, Oklahoma, under Contract No. F 33615-73-C-4013 for the Air Force Materials Laboratories of Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Dr. L.C. Greene, AFML/LPO, is the technical monitor of the contract.

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## INTRODUCTION AND SUMMARY

The purpose of the work under this contract was to develop improved techniques for the production of Group II-VI compound semiconductor materials of higher purity. The general approach was the preliminary purification of the constituent elements using the most effective means for each element and the subsequent synthesis of the compound by reacting the appropriate elements in such a way as to prevent contamination. A second objective of this contract was to carry out an investigation of the growth of both pure and doped II-VI compound crystals from the melt. Crystal growth of these compounds was accomplished by melting the materials in a pressurized furnace containing an inert gas and cooling the melts in a programmed manner to achieve single crystals. This study included the investigation and evaluation of those parameters affecting such variables as polycrystallinity, cracking, twinning and dopant distribution. Crystals produced in this phase of the program were sent to AFML for study and evaluation as requested. Pure compounds were also sent to AFML as required.

The synthesis of ultra high purity II-VI compounds could only be accomplished by using the utmost care in all steps of the operation. The use of high purity elements was the starting point, followed by careful preparation of the apparatus and attention of a skillful operator during the reaction period. Care was taken during the removal and subsequent storage of the synthesized product to prevent any contamination. The material was sealed in small lots of approximately 200 grams in separate polyethelene bottles so that the chance of contamination during final use was reduced to a minimum.

The syntheses of high purity CdSe, CdS, and ZnSe, were carried out in the large three zone vapor phase reactor furnace. The CdSe produced showed a decline in impurity levels from previous runs with the result that no iron or silver were detected in this material.

The main synthesis efforts were concentrated in the ZnSe area. Various experimental efforts were made which lead to the desired results of improved purities and better yields. The use of the "butterfly" rod was successful

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in breaking up the tunnel formation and caused more of the ZnSe to concentrate in the front portions of the reaction tube. The use of the clear quartz liner within the reaction tube reduced the amount of silicon contamination and also facilitated the removal of the final product. No impurities were detected by the emission spectograph in 8 out of the 17 ZnSe synthesis runs made during this period.

The growth of crystals from the melt in the pressure furnace system was carried out on ZnSe, CdS, and ZnTe. The major emphasis of these melt growth runs was the growth of improved structural quality ZnSe crystals, both doped and undoped. Other areas investigated concerned the effects of the crucible's shape and material of construction upon the resulting ZnSe ingots was also an important segment of the study. Over half of the ZnSe ingots furnished to AFML were custom doped with various impurities.

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## II. SYNTHESIS OF HIGH PURITY COMPOUNDS

### A. SYNTHESIS OF CADMIUM SULFIDE

The method of synthesizing cadmium sulfide consisted of reacting the vapors of elemental cadmium and sulfur in a fused silica reaction tube in the temperature range of 1000°C to 1050°C. The synthesis furnace, which was constructed to operate within this temperature range, consisted of a main heating unit approximately forty-four inches in overall length and with a core diameter of 5 inches inside diameter. Forty-two inches of the length were a coiled heating element, while the remaining two inches were sheets of one-inch thick transite insulation on both ends of the furnace. The heating elements were divided into three zones so that different areas of the furnace could be maintained at the optimum temperature for a particular synthesis run. The center zone was thirty inches in length while the front and end zones were six inches.

This three-zone furnace accommodated a reaction tube of fused silica, sand finished on the outer surface and glazed on the inside. The tube was forty eight inches in length and with an outside diameter of three and three quarters inches and with a one fourth inch thick wall. One end of this reaction tube was sealed with a clear quartz disc and from this disc the cadmium and sulfur boiler connection arms extended. The cadmium arm extended horizontally and the sulfur arm bent 90 degrees downward.

The cadmium vapor passed through a small orifice as it entered the reaction chamber. The increased velocity of the cadmium vapor as it passed through the orifice helped prevent the formation of cadmium sulfide in the immediate vicinity of the cadmium inlet, thereby reducing the possibility of plugging the entrance with deposited CdS.

The cadmium boiler was welded to the reaction tube so it was able to withstand back-pressure produced by the orifice. The cadmium boiler was about five and three fourths inches long and the heater was approximately 14" long. The added length insured a more constant temperature control and covered the boiler and the vapor arm completely flush to the plate of the reaction tube.

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The sulfur boiler sat upright on a jack at a ninety degree angle to the reaction tube. It was five and one half inches long and three inches in outside diameter, fitting into a heating element of about four inches inside diameter.

Argon was used as a carrier gas and entered both boilers through small quartz gas flow arms. Both gas flows were monitored by flowmeters, and any pressure buildup in the unit was measured by a liquid mercury manometer mounted in a bypass system on each gas flow line. The argon was purified before being split into the two flows by passing the gas through a titanium sponge heated to $900^\circ C$ which effectively removed the oxygen impurities.

The cadmium boiler operated at approximately $800^\circ C$ while the sulfur boiler temperature was maintained near $500^\circ C$. A quartz baffle was placed near the exit end of the reaction tube to minimize the carry-over of the synthesized CdS. A condenser section at the end of the reaction tube served as a trap for the excess unreacted vapors. This fused silica condenser was sealed to the exit end of the reaction tube with wet asbestos. Its dimensions were four inches inside diameter by twelve inches long and one fourth inch wall thickness. The end of the condenser was capped with a three-sixteenths inch thick clear quartz disc with a centered one inch diameter opening in which a stopper was placed, restricting the gas exit to about one fourth inch. The stopper could be removed and a quartz rod introduced to dislodge material plugging the area around the baffle when necessary.

The reaction tube and its boilers are shown in figure 1.

Temperature control of a cadmium sulfide run was accomplished by the use of five pyrometers and five powerstats. Each powerstat controlled one zone of the reaction zoneheater, or one of the boilers. The operator's visual monitoring and adjustment of these powerstats along with adjustment of the gas flows controlled the unit's operation and form of the final product.

In order to achieve any significant degree of purity of the final synthesized compound, careful attention was paid to details concerning all steps of the purification and synthesis techniques. The reaction tubes,
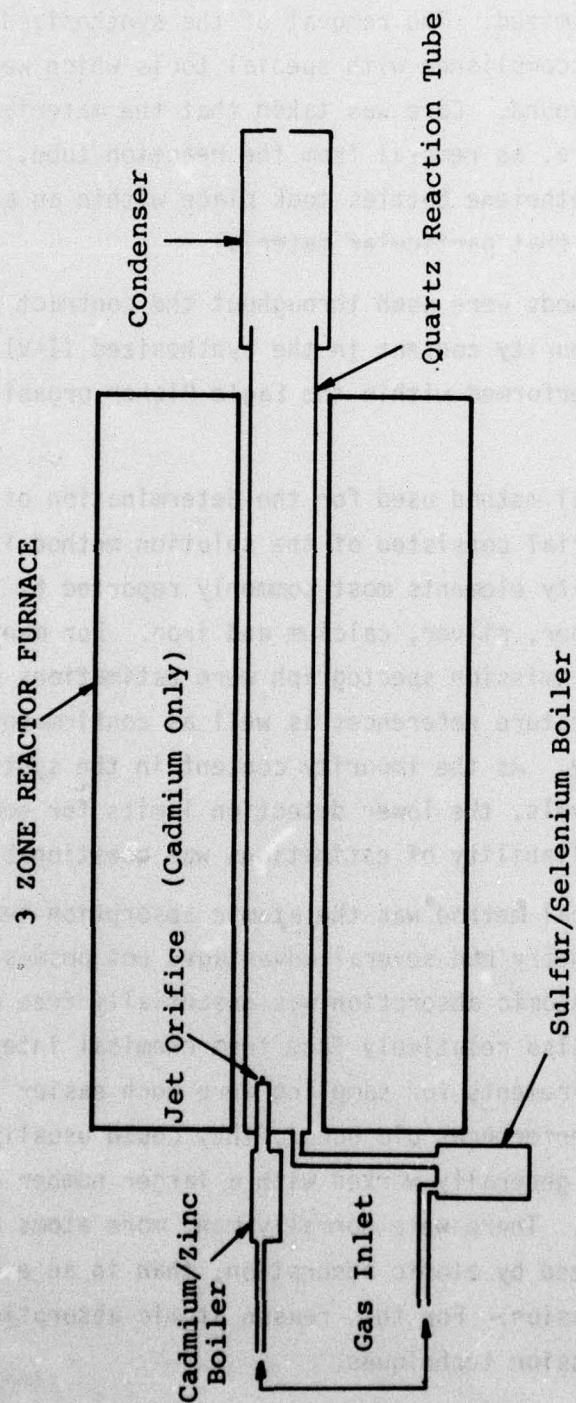
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Figure 1. Schematic of II-VI Compounds Synthesis Unit

boilers, and related quartz apparatus were carefully cleaned, thoroughly rinsed with deionized water, and stored in such a manner that contamination from any source was minimized. The removal of the synthesized product from the reaction tube was accomplished with special tools which were used only for that particular compound. Care was taken that the material was not exposed to the atmosphere, as removal from the reaction tube, sampling and bottling in sealed polyethelene bottles took place within an argon-filled glove bag used only for that particular material.

Two analytical methods were used throughout the contract period for the determination of the impurity content in the synthesized II-VI compounds. These techniques were performed within the Eagle-Picher organization, although at separate facilities.

The first analytical method used for the determination of impurities in the synthesized material consisted of the solution method in the emission spectograph. The impurity elements most commonly reported by this method were silicon, magnesium, copper, silver, calcium and iron. For many elements the detection limits on the emission spectograph were estimations only, and were based on available literature references as well as confirmatory work in the spectographic laboratory. As the impurity content in the synthesized material was reduced to lower levels, the lower detection limits for some elements had been reached and the reliability of estimations was questionable.

The second analytical method was the atomic absorption technique. Atomic absorption spectrophotometry had several advantages not possessed by the emission spectograph. Atomic absorption was essentially free of spectral interferences. It was also relatively free from chemical interferences simply because the requirements for sampling were much easier than in emission work; when chemical interferences did occur, they could usually be eliminated. Also, atomic absorption generally worked with a larger number of atoms than did emission techniques. There were normally many more atoms available in the ground state, utilized by atomic absorption, than in an excited state, were available for emission. For this reason atomic absorption was usually more sensitive than emission techniques.

The major disadvantage with atomic absorption was one of dilution. The sample had to be in an aqueous or liquid medium. Therefore, some dilution inevitably occured and the quantity of the element being determined was reduced by the dilution factor. For example, if a material contained 1 ppm and was diluted 1 to 10, the amount to be actually determined was only 0.1 ppm. This disadvantage could usually be circumvented by utilizing extraction techniques. Impurities specifically detected by this technique were: calcium, copper, magnesium, iron, cadmium, zinc, nickel, potassium and sodium.

Prior to the present contract period, a third analytical method, the mass spectograph, had been employed. This analytical work was conducted under the direction of Dr. Robert K. Willardson at the Bell & Howell Electronic Materials Division at Pasadena, California, for the Aerospace Research Laboratories. The mass spectrographic technique offered the advantages of much lower detection limits and the ability to detect anion as well as cation impurities. With reference to the same impurities found in the other two methods, specifically: sodium, magnesium, potassium and calcium, all were determined by the mass spectrograph to be less than reported by factors of from 10 to 100, except calcium which was very close to the same value as in these previous studies.

There was only one cadmium sulfide synthesis run made during this period. This was in contrast to ten runs made during the period covered by the last interim report. A shift in material requirements and emphasis by AFML to zinc selenide accounted for this lessened effort on cadmium sulfide as the contract drew to an end.

During cadmium sulfide synthesis, the main reaction temperature was maintained at 975°C. The cadmium boiler temperature was 780°C while the sulfur boiler temperature ranged from 475° to 495°C. After the run was finished there was approximately 25 grams of elemental sulfur remaining in its boiler. This heel was a good yellow color but there were some black "organic hydrocarbon" rings left on the sides of the boiler. The cadmium boiler contained a small CdO residue, but the amount was well within the expected quantity.

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The synthesized cadmium sulfide amounted to 715 grams and consisted mainly of needles and platelets with a moderate amount of powder throughout the reaction zone. There was a large amount of fines in the condenser along with a small amount of free cadmium. A small vertical wall of cadmium sulfide was noted in one area. The formation of this wall was unusual in CdS runs and may indicate an area of lower temperature in the reaction zone.

TABLE I

IMPURITIES IN CADMIUM SULFIDE

(Emission Spectrographic Analysis-Data in ppm)

|  | Si | Mg | Pb | Cu | Ca |
|---|---|---|---|---|---|
| CdS Lot #378 | .38 | .08 | 5.4 | .03 | .03 |

B. SYNTHESIS OF CADMIUM SELENIDE

Cadmium selenide was synthesized in the same manner as cadmium sulfide. The position normally occupied by the sulfur boiler was taken by a fused quartz selenium boiler which was welded into place to provide a leak-proof seal. The position of the selenium boiler necessitated the use of a fairly long vapor transfer tube which acted as a reflux column and resulted in a rather slow introduction of selenium into the reaction chamber. The rate of combination of the elements was rapid, as during most synthesis runs 90% of the product was recovered within the first half of the reaction tube. The flow rates of the cadmium and selenium vapor were kept as balanced as possible so that the least amount of excess elemental vapor would be carried to the condenser.

It was found that the combined flow rate, and to a lesser extent the reaction zone temperature, had a marked effect on the physical form of the synthesized product. Between 1000°C and 1050°C the cadmium selenide was produced as a fine crystalline powder while at temperatures over 1050°C the synthesized material formed substantially crystal platelets, large clusters and hollow prismatic needles, other conditions remaining the same. By varying the master carrier gas flow rate at run temperatures of 1000° to 1065°C, it was

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demonstrated that a dense product containing mostly needles was produced using a flow rate of approximately 1.8 cu. ft. per hour argon, while utilizing a rate of about 2.5 cu. ft. per hour argon produced crystalline powder of dense or light composition with no needles.

The analytical results of these cadmium selenide synthesis runs are found in Table II. From the analyses, impurity differences were not significant enough to demonstrate the preference of one type (needles or powder). Preferences could only be made with respect to material application. The powder form was more suitable for melt-crystal growth as it allowed the crucible to be filled without first crushing the charge as would have been required if it were in the needle form. The needle form was well suited for vapor-phase growth as it allowed a more free gas flow and surface sublimination.

CdSe Run #60 was operated at a lower flow rate than Run #59 and, as previously noted, this contributed to the formation of needles and little powder. Runs #59 and #61 demonstrated that the fine powder could be produced at higher carrier gas flow rates. (Twelfth Progress Report)

An interesting vertical tunnel was noted in Runs #60 and #61. It continued from the Cd inlet to the end zone in both runs. (Twelfth Progress Report)

In Run #61, the Se was thought to be the limiting factor of the elements, and as such, was operated slightly in excess. The result was no free Cd at the baffle, and a record recovery was made.

The analytical results continue to show the decline of impurity level from those near the beginning of the contract period. Of particular note is the low level of Fe and Ag and very low levels of Cu and Mg by the Emission Spectrograph.

C. SYNTHESIS OF ZINC SELENIDE

The production and improvement of zinc selenide powder received the most emphasis with seventeen synthesis runs made during the reporting period. The synthesis of zinc selenide was accomplished in a similar manner as cadmium

selenide, by the reaction of the elemental vapors. Both the zinc and selenium were used as received from the suppliers for synthesis.

Zinc selenide synthesis runs appeared to be especially sensitive to operational difficulties. Because the zinc was so reactive, the purity and dryness of the carrier gas was extremely important. Even a small amount of oxygen or water vapor caused a deposit that obstructed the zinc vapor stream. A molecular sieve in addition to the titanium oxygen-getter was used for argon purification. The selenium boiler operating temperature was approximately 750°C and a small change in temperature radically affected the flow rate of the selenium vapors entering the reaction chamber. This was principally due to the tendency of the selenium to reflux in the quartz inlet arm. It was also noted that the ZnSe synthesis runs caused more severe devitrification of the silica reaction tube than the other materials. A reaction tube would be reused only a few times before small chips from the surface contaminated the ZnSe. In addition to the devitrification, free zinc sometimes froze out near the baffle and wetted the silica and broke off pieces from the surface.

The zinc selenide synthesized mainly in the form of fine, crystalline yellow powder. In some cases, the zinc selenide deposited in the form of a tunnel within the reaction tube, starting at the zinc vapor inlet and growing from that point along the length of the reaction tube to the baffle. The propensity of zinc to combine with selenium was very great, and the rapidity of the reaction created a tunnel, with the immediate combining of the elements extending the walls of the tunnel continuously. The reaction was an exothermic one, and the progression of the tunnel was followed by observing the rise and fall of the three zone pyrometers as the building tunnel approached and passed them. The temperature rise indicated by the pyrometer was as much as 50°C, but could be reduced by the operator reducing the zone power or flow rate. This reduction apparently reduced the tunnel formation. When the tunnel reached the rear baffle it split and the vapors went into the condenser to deposit, either as fines or molten elemental zinc and selenium.

Several innovations and departures from normal were investigated. As

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stated, when the zinc froze in the reaction tube it cracked and strained the silica in such a manner that $SiO_2$ flakes contaminated the synthesized material when it was removed. This problem was partly remedied by replacing a one foot section from the end of the reaction tube, the area most susceptible to damage, on a regular basis. A better solution was the use of clear quartz liners placed inside the reaction tube to contain the material. (See figure 1)

In addition to the procedures and apparatus adapted during the previous interim period, several innovations and departures from normal were investigated.

ZnSe Run #104 (Ninth Progress Report) utilized the double-half-baffle system and no rear baffle. (See figure 2) Visual observation to the front plate of the silica reaction tube was possible. During the initial stages of the run, it was possible to see the vapors and adjust any imbalance. Later, the progress of the building tunnel was observed on the zone parameters. A Leeds and Northrup optical pyrometer was used during this run by sighting down the length of the reaction tube, and the agreement with the normal thermocouple-type was within 1%.

In the next run, #105 (Ninth Progress Report), a return to the "butterfly" rod and full baffle was made. (See figure 2) A new fused silica condenser was introduced as replacement for the iron one previously used. The new condenser was four and one half inches outside diameter by twelve inches long. The rear plate was of three-sixteenth inch thick clear quartz and contained a hole for the neoprene stopper. The new condenser lessened the possibility of contamination from previous runs, as it was cleaned much more easily than the old one. Also, the new condensor did not conduct heat during the run. In addition, the clear plate provided good visibility and a wide angle access to the reaction chamber to evaluate conditions at the start of the synthesis run.

During the subsequent runs, the "butterfly" rod was successfully used. Both rotational and longitudinal motion was used to break up the forming tunnel. This achieved a significant increase in the amount of synthesized material recovered.

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**DOUBLE – HALF BAFFLE**

16"

6 mm ROD

3" DIA. x 1/8"

**BUTTERFLY ROD**

48"

2 1/4" DIA. x 1 1/8"
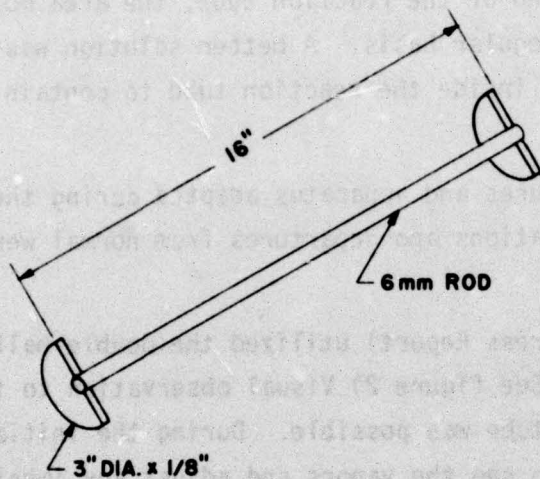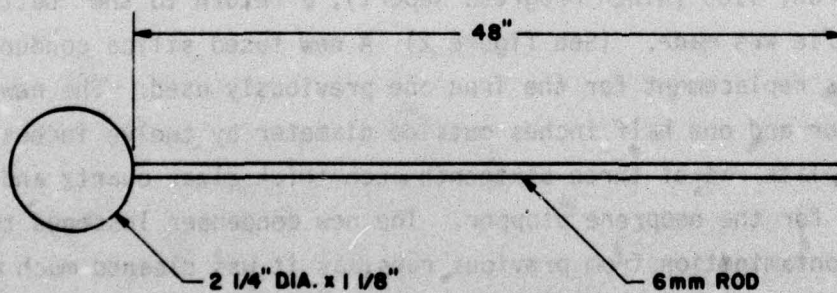
6 mm ROD

FIGURE 2: DOUBLE – HALF BAFFLE AND BUTTERFLY ROD

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Also, the use of the clear quartz 70 mm liner was extensive, as it facilitated removal and observation of the material growth characteristics. It also allowed cool down under an argon stream and reduced the contamination of silicon and other impurities from the lower grade reaction tube.

A problem in Run #110 (Tenth Progress Report) was a broken connection causing the loss of one-quarter of the center zone heater. This was remedied as the power to that zone was increased to compensate for the loss, and normal operating temperatures were achieved. This was an intermittent problem until the top half of the center zone was replaced with a new heating unit.

Due to the withdrawal of the "butterfly" rod during the synthesis runs, occasionally the rear baffle was pulled back into the condenser area, allowing some discoloration of material in latter part of the reaction tube. In ZnSe Run #114 (Eleventh Progress Report) and in subsequent runs, the baffle was anchored by welding a length of two millimeter quartz rod between the liner and the baffle.

In Runs #115 and #116, (Twelfth Progress Report) the boilers were charged with excess in the hopes of verifying Se as a limiting factor of the reaction stoichiometry. However, only a slight excess could be maintained due to the tendency of Se to discolor the product. Nonetheless, the recovery percentages and total ZnSe recovered were the highest recorded thus far in the contract.

Analytical analyses for the ZnSe synthesis runs made during this report period are found in Table III.

Careful attention was paid to the many details concerning all steps within the purification and synthesis technique. When the impurity levels neared the detection limit, it became even more difficult to resolve differences between runs and so evaluate the results of any change of the synthesis technique.

As seen in Table III above impurities were seldom detected with the Emission Spectrograph. As seen in the Atomic Absorption data, the impurity levels of certain elements decreased steadily throughout the period of the contract.

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## TABLE II

### IMPURITIES IN CADMIUM SELENIDE

#### (Emission Spectrographic Analysis - Data in ppm)

| Lot No. | Ca | Cu | Fe | Mg | Ag | Si | Pb | Zn |
|---------|------|------|------|------|------|------|------|------|
| 59 | ND | .010 | ND | .011 | ND | 1.1 | ND | ND |
| 60 | ND | .038 | ND | .024 | ND | 2.3 | 1.1 | ND |
| 61 | ND | .026 | ND | .023 | ND | 2.0 | 1.9 | ND |
| 62 | ND | .062 | .50 | .056 | ND | 1.1 | ND | ND |
| 63 | ND | .05 | ND | .02 | ND | .5 | 2.6 | ND |
| 64 | ND | .11 | .3 | .04 | ND | 1.5 | 2.8 | ND |

#### (Atomic Absorption Analysis - Data in ppm)

| Lot No. | Ca | Cu | Fe | Mg | Ni | Zn | K | Na |
|---------|------|------|------|------|------|------|------|------|
| 59 | 1.7 | .13 | 2. | .62 | .52 | – | .57 | 2.3 |
| 60 | .23 | .93 | .51 | .11 | .25 | .19 | .18 | .33 |
| 61 | .23 | .05 | 1.5 | .14 | .25 | .19 | .18 | .46 |
| 62 | 1.1 | .26 | .88 | .54 | .88 | .05 | .58 | 3.7 |
| 63 | 1.1 | .55 | 3. | .95 | .96 | .23 | .2 | 2.9 |
| 64 | 1.4 | .08 | 3. | .62 | .83 | .07 | .2 | 1.2 |

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## TABLE III

### IMPURITIES IN ZINC SELENIDE

(Emission Spectrographic Analysis - Data in ppm)

| Lot No. | Ca | Cu | Fe | Mg | Ag | Si | Pb | Cd |
|---------|------|-----|-----|-----|-----|-----|-----|-----|
| 103 | ND | ND | ND | ND | ND | ND | ND | ND |
| 104 | ND | ND | ND | .5 | ND | 2.3 | ND | ND |
| 105 | ND | ND | ND | .6 | ND | 3.2 | ND | ND |
| 106 | ND | ND | ND | ND | ND | 3.0 | ND | ND |
| 107 | ND | ND | ND | ND | ND | ND | ND | ND |
| 108 | ND | ND | ND | ND | ND | ND | ND | ND |
| 109 | ND | ND | ND | ND | ND | ND | ND | ND |
| 110 | ND | ND | ND | ND | ND | ND | ND | ND |
| 111 | .2.0 | ND | ND | ND | ND | ND | ND | ND |
| 112 | <.5 | ND | ND | ND | ND | ND | ND | ND |
| 113 | ND | ND | ND | .5 | ND | 2. | ND | ND |
| 114 | ND | ND | ND | .5 | ND | 2. | ND | ND |
| 115 | ND | ND | ND | ND | ND | ND | ND | ND |
| 116 | ND | ND | ND | ND | ND | ND | ND | ND |
| 117 | ND | ND | ND | ND | ND | ND | ND | ND |
| 118 | ND | .5 | ND | ND | ND | ND | ND | ND |
| 119 | ND | ND | ND | .7 | ND | 2.5 | ND | ND |

# TABLE III (CONT'D)

## (Atomic Absorption Analysis - Data in ppm)

| Lot No. | Ca | Cu | Fe | Mg | Ni | Cd | K | Na |
|---------|------|-----|-----|------|-----|------|-----|------|
| 103 | 1.5 | .16 | .93 | .21 | .67 | .3 | .67 | 1.0 |
| 104 | 3.27 | .33 | .96 | .21 | .67 | .8 | .87 | 1.2 |
| 105 | .2 | .16 | .74 | .18 | .82 | 1.7 | .67 | 2.4 |
| 106 | .14 | .18 | .81 | .14 | .23 | .83 | .06 | .53 |
| 107 | .14 | .13 | .87 | .14 | .23 | 1.04 | .06 | .57 |
| 108 | .3 | .09 | .4 | .04 | .7 | .6 | .5 | 1.2 |
| 109 | .4 | .1 | .2 | .04 | .3 | .3 | .3 | 1.3 |
| 110 | 1.3 | .7 | 1.1 | .65 | .2 | .3 | .12 | 2. |
| 111 | .2 | .1 | .5 | .16 | .2 | .5 | .06 | .5 |
| 112 | 1.3 | .45 | 1.1 | 1.4 | .23 | .12 | .51 | 1.7 |
| 113 | .75 | .17 | 1.8 | .26 | .75 | 1.5 | .39 | 1.2 |
| 114 | .75 | .17 | 1.8 | .26 | .52 | 1.5 | .39 | 1.0 |
| 115 | .26 | .3 | .98 | .23 | .75 | - | .62 | .80 |
| 116 | .17 | .3 | .89 | .13 | .97 | - | .62 | .76 |
| 117 | .15 | .14 | 1.5 | .29 | .38 | 1. | - | .19 |
| 118 | .12 | .08 | 1.5 | .19 | .11 | - | .68 | .6 |
| 119 | 1. | .14 | 2.6 | .4 | .3 | 2.6 | .38 | 2.2 |

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## SECTION III

## GROWTH OF CRYSTALS

### A. PRESSURE MELT GROWTH

The growth of ZnSe from the melt in the pressure furnace continued to receive special attention. In addition to runs made to supply AFML with 81 melt grown ZnSe crystal ingots, many other experimental runs were conducted to improve the crystal structure of the melt grown ingots. A few series of ZnTe melts were also made for the production of 48 ingots for AFML, both undoped and doped. A total of 14 ingots of CdS were also made at the specific request of AFML.

#### 1. Zinc Selenide Crystal Growth

At the beginning of this period it was necessary to clean and overhaul the pressure furnace. The heater and thermocouple were both replaced. After such maintenance it was necessary to re-establish the melting point and best instrument parameters for this new set of thermocouple and heater. The pressure furnace and its puller mechanism is shown in figures 3 and 4.

The process of determining the basic growth conditions involved a time consuming experimental program that prevented any serious growth experiments until these had been definitely established. It took weeks to find even the proper range. The melt temperature was one of the main considerations but by no means the only one. The relationship of the crystal growth interface to its position in the crucible was also of critical importance. Thus the cooling rate and crucible lowering rate both had a pronounced effect on the final crystal quality and these factors also needed to be re-established after thermocouple replacement was made.

In past runs it had been noted that many of the good ZnSe ingots had a top surface which showed no grain boundaries over 90 to 95% of the surface area, and with a small cluster of polycrystalline grains near one edge of the ingot. The crucible was then marked so that it could be oriented in the same position in the furnace for each run. The location of the polycrystalline areas were then
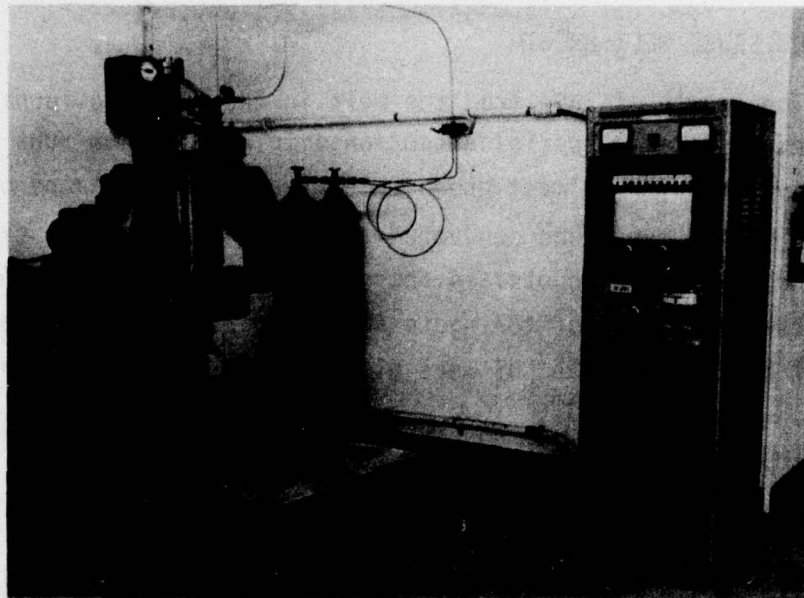
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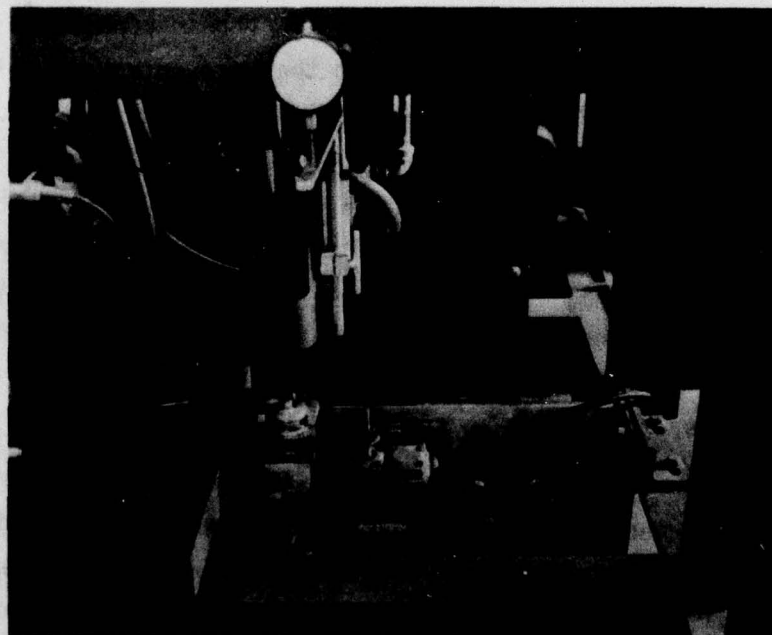.Figure 3.   Melt Growth Pressure Furnace



Figure 4.   Puller Mechanism on Pressure Furnace

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related to their position relative to the internal surface of the crucible and to their position relative to the heater. This was done to ascertain whether the most influential factor in the formation of the small polycrystalline clusters was the crucible or the thermal pattern from the heater and insulation. After each run, the orientation of the resulting ingot was marked with a felt pen. Then, after sandblasting the top surface of the ingot to delineate the crystal grains, the pattern of the grain boundaries was sketched with the orientation noted. Two kinds of ingots were eliminated from this study. One was the good ingots showing no extra grain boundaries and the other type was the polycrystalline boules which had an abundance of grain boundaries covering the entire top surface. The remaining ingots of the study all had grain boundaries in from one to three quadrants of their top surface. Approximately 67% of the test ingots had multi-crystal areas in the first quadrant, 33% in the second quadrant, and 27% in the third and fourth quadrant. These results indicated that a preference for polycrystal formation existed in the area of the first quadrant. The next step was to rotate the crucible $180^o$ to determine if the crucible was the major factor. However, this experimental series was subject to many qualitative judgements which precluded solid conclusions. In particular, this series was hampered by the fact that the correct or best operating conditions had not been established since the heater and thermo-couple maintenance had been performed. Another factor was that the crucible itself had been used for many months and was becoming badly eroded and worn. Thus it was felt that the experiment would best be repeated after good growth conditions have been established in a newer crucible. This test was not completed by the contract conclusion.

Many factors contributed to the growth characteristics of the final ZnSe ingot, some of which could not be recognized in each individual growth attempt. The effect of the crucible on crystal growth was an important factor. The basic crucible design used for many years generally proved to be the best of the many shapes experimented with (see figure 5). After a certain amount of usage,

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Lid

Body

4" Taper

Base

Plug
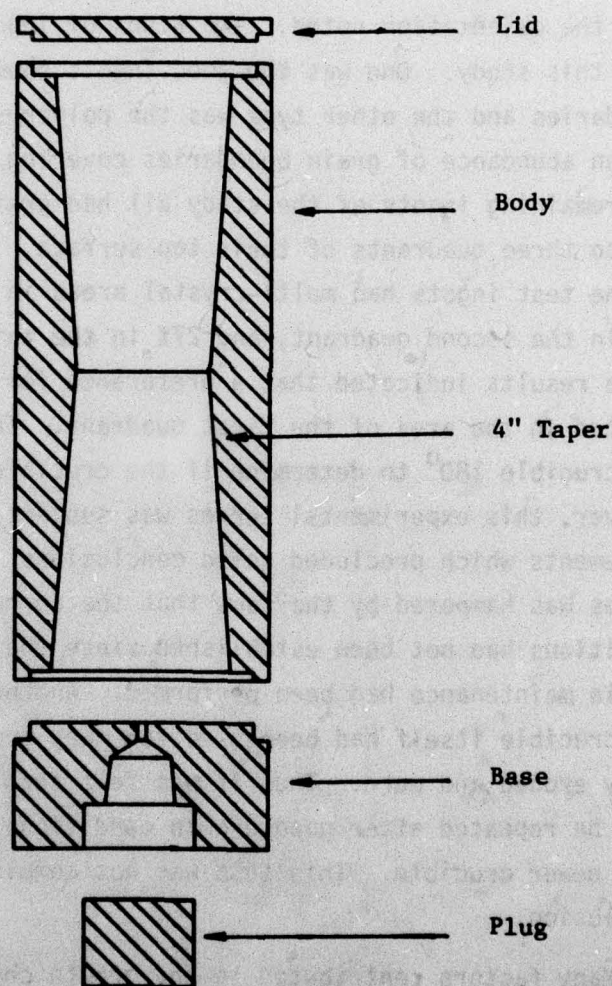
**Figure 5.** New Graphitite Crucible

however, the slow erosion of the inner surfaces of the graphite
crucible had an adverse effect on the resulting crystal growth
that could no longer be compensated for. Then, the crucible was
"worn out" as far as other crystal runs were concerned, even though
the actual dimensions of the crucible were not significantly changed.

In one such instance, a series of crystal growths in pressure
furnace #1 began to deteriorate until the majority of the ingots
contained polycrystalline areas in excess of 60% of the ingot's
surface. The crucible was then transferred to pressure furnace
#2, where recent runs were achieving a fairly good degree of success.
The resulting crystal quality immediately began to decrease, showing
much more polycrystalline areas throughout the crystal ingot.
After this trend was established for 5 runs, changes were initiated
in the growth program to see if the quality of the crystals could
be improved. No change that was tried resulted in any improvement.
It became apparent that once the crucible reached a certain point,
it was no longer suitable for crystal growing. The crucible could
often be remachined on the inside so that it could be successfully
reused but many times even this approach did not yield the desired
results. The "used" crucible could sometimes be used for other
II-VI compounds but generally it was best to discard it and start
over with a new crucible.

The best crucible material tried was "Graph-I-Tite" graphite.
Poco CZR-1 graphite was tried on CdS and ZnS but was unsuccessful
because the resultant crystals were darkened due to contamination from
the crucible. It was decided to try this Poco graphite for the growth
of ZnSe from the melt since ZnSe generally did not attack the
graphite surface of the crucible to a very significant degree.
Three melt runs were made using the Poco graphite crucible. The first
run resulted in a darker ingot and the third run was darker yet.
Even though Poco CZR-1 graphite was a very good grade of graphite
for zoning and crystal growth of high purity semiconductor materials,
it apparently was not acceptable for the growth of II-VI crystals
from the melt.

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In the continuing study of crucible materials a new source of graphite was obtained. This graphite, UT6 grade from Ultra Carbon Corporation, was comparable in purity and density to the graphite normally used for our II-VI crucibles. A new crucible was fabricated from this UT6 graphite for crystal growing trials of ZnSe in the pressure furnace. The first ZnSe melt run yielded an ingot that had a dark maroon color throughout the entire boule. The second ingot was dark maroon in the top half and dark brown in the bottom portion. The next two runs yielded about the same results but then subsequent runs began to show a slight improvement in color. It was decided to continue the growth tests to see if further improvement could be noted. After a total of 15 runs, a definite improvement in color could be seen although a slight discoloration still appeared near the top of the ingot. Samples of three ZnSe ingots were sent to the emission spectro lab for analysis to determine what purity was being leached from the graphite crucible to cause the reddish color in the melt grown ingot. Table IV shows these analytical results.

## TABLE IV
### IMPURITIES IN ZINC SELENIDE INGOTS
(Emission Spectrographic Analysis - Data in ppm)

|                    | Pb | Si  | Mg   | Fe  | Al  | V  | Cu   | Ni  |
|--------------------|----|-----|------|-----|-----|----|------|-----|
| ZnSe Ingot #15200  | ND | 2.  | 0.90 | 7.0 | 6.2 | 6. | 0.38 | 4.9 |
| ZnSe Ingot #15209  | ND | 5.9 | 0.95 | 4.5 | 5.6 | 4. | 0.37 | 1.  |
| ZnSe Ingot #25206  | ND | 2.  | 0.64 | 3.1 | 7.3 | 4. | 0.37 | 1.  |

The first ingot, #15200, had the distinctive darker color, while the second ingot, #15209, had begun to show a lighter color. The third ingot, #25206, was grown in a different crucible and had the characteristic light golden color of normal ZnSe ingots. The darkest ingot had the higher concentrations of Fe, V, and Ni. From past experiences of using dopants of these materials it appeared that the Ni was the impurity most likely to cause a darkening of ZnSe when it is present even in fairly minute quantities. In one instance less than 2 ppm Ni was enough to darken a crystal.

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In conjunction with the request of AFML for cleaved crystal samples, a continuing evaluation of the ZnSe melt grown ingots was made by observing the resultant cleaved pieces. Initially, the cleaving attempts were made using a thin bladed chisel which was struck with a plastic mallet. It was found that this method was not very satisfactory since many cleaved pieces were shattered into smaller fragments due to the force of the striking mallet.

In order to better control the rate at which the crystal cleaves and to refrain the resulting fragment from further damage, the method of cleaving was modified. The modified practice consists of applying a load to a vertically mounted chisel using a hand-operated press. The ingot was hand-held against the base of the press at the angle which appeared to allow the crystal to cleave along its preferred plane. Most ingots were placed flat at $90^{\circ}$ to the cleaving chisel although some ingots seemed to cleave best at an angle of approximately $30^{\circ}$ to the horizontal.

Many times large slabs of the ingot resulted from the cleaving process while at other times only much smaller chips were recovered. In some instances the cleavage was observed as the crack slowly propagated through the crystal as a steady, slow pressure was maintained on the cleaving blade. These instances generally occured when the ingot cleaved into uniformly thick, straight-sided pieces somewhat similar to slices of bread. Closer observation of these pieces indicated that the center portion of the ingot froze very uniformly with only slight disturbances in the growth lines noted near the outside surfaces which were in contact with the crucible walls.

The surface patterns on top of an ingot did not always give a clear indication of how to cleave the ingot. Usually the twin lines were used as a guiding factor in that this type of ingot often cleaved in a direction parallel with the twin lines. This was not always the case, however. Some ingots looked very good on the top surface but were very difficult to cleave, requiring an extreme amount of

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force to be applied to the cleaving blade. The resultant pieces were almost always fragmented and rough along the surfaces. These pieces indicated a rather turbulent growth pattern, heavily influenced by intruding crystal planes nucleated from the crucible sides. A typical ZnSe ingot and a photomicrograph of its surface patterns is shown in figures 6 and 7.

Of the 81 melt grown ZnSe ingots furnished to AFML, 32 were undoped while the remaining 49 were doped with specially requested dopants in varing quantities. The capability of controlled doping of the crystal ingots in the pressure melt process was one of the major advantages of this process. Impurities that otherwise might have vaporized at elevated temperatures at atmospheric pressure often dissolved in the molten II-VI compound at the increased pressures.

Normally, doping runs were made in consecutive order. The crucible was thoroughly wiped out with a towel after the run was over before the fresh powder charge was added. In most instances this cleaning was sufficient to prevent any carry-over of the previous dopant into the next run. There have been a few cases where minute traces of impurities were transferred into the next runs, especially when the initial doping level was in excess of 100 ppm.

Since Na and Li were especially difficult impurities to avoid in the preparation of any compound, it was decided to take extra care in a doping series where it was desired to have as little cross contamination between the Na and Li dopings as possible. In this series, the ingots were handled only with plastic tongs and were carefully sealed in bags to prevent any contamination of the ingot after it was grown. The crucible was cleaned in the normal manner and then an undoped ZnSe melt was made in it to help further reduce any remaining dopant to extremely low levels before the next different dopant was used.

The dopants requested for this series consisted of Na, Li, and Ag as single dopants and then, double dopants combining Al with each of the previously named three elements

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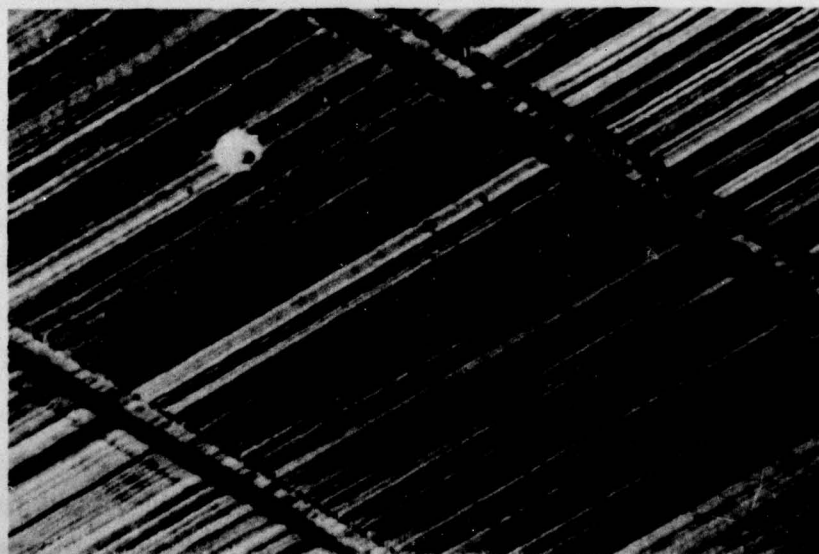
Figure 6. Zinc Selenide Crystal With Cleaved Face



Figure 7. Twin Bands on ZnSe Crystal (200X)

The 100 ppm Na dopant made no visible change in the ZnSe ingot. The addition of 100 ppm Al to the same amount of Na gave a yellow orange color with a slight reddish deposit on the top surface of the ingot. The 100 ppm Li doping yielded an ingot which was lime green in the bottom half while being darkened and cloudy in the top half. The addition of 100 ppm Al to an equal amount of Li resulted in a uniformly clear lime green ingot. The Ag doping yielded a dark brown colored ingot at 100 ppm Ag and a lighter brown at the 10 ppm Ag level. The combination of 100 ppm Ag with 100 ppm Al gave a bright orange coloration to the ZnSe ingot. It seems that usually whenever Al was used it gave the dominant color to the resulting ingot, probably because up to 100 ppm Al was quite soluble in ZnSe, being uniformly distributed from top to bottom.

Three other ingots were doped with Ga at 50 ppm. Two of these were double dopings, the first with 50 ppm Na and the second with 10 ppm Li. All the ingots were fairly uniform and cleaved into nice pieces. The single Ga doped ingot did show a slight darkening at the top surface that could be the result of slight segregation or improper mixing of the dopant.

Another series of ingots was doped with 50 ppm In, with two double dopings. One contained 50 ppm Na and the other was doped 10 ppm Li. The In doping caused a slight brownish color in the ingots but the additional Na and Li seemed to make no significant change. The In + Na ingot was much harder to cleave than the others and yielded smaller pieces, indicating a more polycrystalline ingot.

Another doping series was made with silver as the impurity. The 300 ppm Ag doping yielded an opaque dark black ingot. The ingot was cleaved into small pieces after the run at the request of AFML to supply the size of crystalline pieces they need for their experiments. Approximately half of the ingot cleaved into useful pieces while the remaining half was more polycrystalline and fragmented into poorer chunks. The 200 ppm Ag ingot cleaved into vertical

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slices with smooth surfaces. This indicated that the interior crystal-
linity of the ingot was very uniform from bottom to top. The 100
ppm Ag ingot and the 30 ppm Ag ingot both cleaved into pieces. The
color of the pieces was uniform throughout, indicating that the
dopant was evenly distributed with no visible segregation at the top
or bottom of the ingot. A crucible clean-out run was made following
the final Ag doping so that any remaining dopant would be removed and
would not carry over as a contaminant in subsequent melt growth attempts.
This clean-out yielded an ingot which contained an extremely low level,
less than 1 ppm, of the dopant, which was sent to AFML.

Another doping series was made using isotopic Ag-109 at 200 ppm,
100 ppm, and 30 ppm levels. This isotopic Ag was supplied by AFML
especially for this series. The resulting ingots were comparable
to the previous Ag doped runs. The ingots all cleaved easily and
*yielded uniform pieces. The crystallinity was good on all the ingots.*
The thinner pieces were transparent with a blackish-green coloration.

Following a standard crucible clean-out run, another doping series
was initiated using a double dopant combination of Ag + In. The Ag
concentration was 3 times the concentration of In and varied from 30
ppm to 200 ppm. These ingots were all dark and opaque due to the added
dopants. The cleaving results were all satisfactory although a few
of the ingots cleaved at an angle of approximately 30$^{\circ}$ to the vertical.

2. Zinc Telluride Melt Growth

A total of 26 undoped and 22 doped ingots of ZnTe were shipped to
ARL this period. These were the first ZnTe ingots to be doped on this
contract.

Zinc telluride melted at approximately 1300$^{\circ}$C. The compound
was synthesized from the elements in the pressure furnace and the
resulting ingot was crushed into powder for use in subsequent melt
crystal growth runs. Zinc telluride had a greater tendency to de-
compose than ZnSe, so some changes were necessary to reduce these
effects. Zinc telluride was grown in a sealed crucible at pressures

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exceeding 1000 psi. The resulting ingots were polycrystalline, but contained fair-sized crystal areas. The ingots were dark maroon in color and almost opaque. However, they were clear and transparent to a strong light source. Thinner slices were quite transparent and were polished to a good surface finish.

The dopants used in the ZnTe melts consisted of 100 ppm Na, 100 ppm Ag, 50 ppm Al, 50 ppm In, 50 ppm Ga, and 10 ppm Li. Because of the dark intense color of the ZnTe, it was difficult to observe any change due to the added dopant. All seemed to be dissolved completely and no segregation was noted. The Al doped ingot was the only one that appeared to be changed to any extent. The color of this ingot was a brighter reddish-maroon and seemed to be especially clear.

These ZnTe ingots were cleaved into smaller pieces before shipment. The method of cleaving was the same as is used on the ZnSe ingots. The ZnTe ingots generally cleaved more easily than ZnSe. Slabs were also cleaved horizontally across the ingots.

Vertical cleavage was also possible on some ingots if the ingot orientation was correct. Ingot ZnTe #15275, cleaved vertically this period, yielded a section which extended the entire length of the boule. The cleaved face of this piece was straight and smooth over approximately 90% of the section's length. A faint plane of parallel lines were seen running nearly vertically with only slight variations in direction until they reach a point 2 mm from the top surface. At this point the growth lines uniformly swerved to the side, indicating the final freezing pattern at the top surface of the ingot. The surface patterns on this cleaved section certainly indicated a smooth, uniform freezing of the ingot during its cooling period with almost perfect nucleation of the crystal at the beginning. Unfortunately, subsequent runs using the same growth programs did not succeed in duplicating this almost perfect crystal formation.

A new ZnTe synthesis crucible was made which fitted more uniformly in the heater of the pressure furnace. The crucible consisted of a vitreous carbon container one and onehalf inches in diameter by three and onehalf inches high. The volume of the crucible is sixty-six ml which was large enough to synthesize 200 grams of ZnTe per run.

The new crucible fitted within the standard crucible space and did not require the special "short" thermocouple to be installed in the furnace as the previous crucible did. This eliminated the necessity of re-establishing the melt point as was always required when the thermocouple is changed in the furnace. The first results from the use of the new synthesis crucible were encouraging. It appeared that the material synthesized in a very uniform manner and no segregation or voids were noted. The ingots were crystalline and the color was uniform. The ingots did not stick to the crucible but were easily removed for crushing into smaller pieces.

### 3. Cadmium Sulfide Melt Growth

During the last quarter of the contract all the pressure furnace runs were aimed at the production of specifically doped crystals of cadmium sulfide at the request of AFML. A total of 14 cadmium sulfide ingots, 13 of which were doped, were shipped to AFML.

First a series of undoped CdS ingots were grown to establish the proper melting point and best cooling program to be used in the growth of acceptable ingots. The growth of good single crystals of Cds from the melt was achieved with reasonable success but these ingots, especially if another crystalline is present in the boule, were especially subject to strain cracking. However, since it was requested that the crystals be cleaved prior to shipment to AFML, a small amount of cracking was not detrimental to these ingots.

The doped series was begun with a series of Li dopings. The ingot was doped with 1 ppm Li. A good crystal was grown but it was dark in color, probably from carbon inclusions. The ingot cleaved poorly, yielding fragmented pieces. The proper cleaving angle was not found on this ingot but the resulting fragments were of useable size.

The next ingot was doped with 3 ppm Li. Again the cleaving angle was hard to find. The resulting slices were thin and fragile. The color of the ingot was improved, however.

A 10 ppm Li doping yielded a good crystal of uniform appearance.

The ingot cleaved very easily into nice, thin full cross-section
pieces. This was followed by an undoped CdS melt to be used as a
crucible cleanout run. The resulting ingot can be used as an extremely
low level Li doped crystal.

The next series of CdS runs were dedicated to Na dopings. The
first ingot was doped with 3 ppm Na. This ingot broke easily with the
resulting slices having smooth faces parallel to the twin lines.

The 10 ppm Na doped ingot appeared to consist of 2 or 3 crystallites.
The color was uniform with no evidence of dopant segregation. Cleaving
the ingot resulted in a few full cross-sectioned slabs.

The last ingot of the series, 30 ppm Na, cleaved easily although
the resultant pieces were not flat and smooth but appeared wavy and
striated. The lines indicated an uneven cooling cycle during the
crystal growth period.

The final series of the doped CdS runs consisted of Ag dopings.
The first level of 10 ppm Ag yielded a reddish orange ingot. The ingot
was cleaved at an angle of $20^0$ from the vertical. The slices were
slightly darker at the top of the crystal boule.

The 30 ppm Ag doped ingot was quite a bit darker in color than the
previous ingot and had some internal cracking. The ingot cleaved
into rough pieces, yielding only small fragments. Once again the color
was darker near the top of the ingot, indicating some nonuniformity
in dopant distribution.

The 100 ppm Ag doped ingot was nearly opaque. The ingot broke
easily but yielded only rough faced pieces.

The final ingot was double doped with 10 ppm Na and 30 ppm Ag.
The color of the crystal was red-orange with no cracks visible. The
cleavage plane was found by rotating the crystal and successively
applying light pressure to the cleaving blade. The slices broke
easily, yielding uniformly colored pieces containing a few striations.
A final crucible clean-out run was included with the best shipment of
material.

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